Communication

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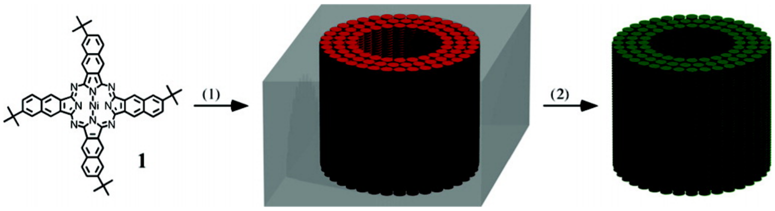

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Nanotubes Fabricated from Ni−Naphthalocyanine by a Template Method

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Graphitic carbon nanotubes (GCNT) are attractive because of their unique electronic properties and many potential applications.[1,2] Chemical vapor deposition (CVD),[3] arc-discharge,[1,4] and laser ablation[5] have been used for their preparation. While the graphene layers of GCNTs are known to be oriented along the tube axis, a new type of GCNTs would arise if these sheets were perpendicular to the tube axis, forming the walls like brick layers. This suggests fabricating GCNTs from graphene molecules as building blocks rather than from gaseous C_2 units, as in the above methods, and indeed, graphene sheets of hexa-*peri*-hexabenzocoronenes (HBCs)[6] have been assembled into tubes from solution.[7] However, the mode of binding and the presence of “soft” alkyl chains limit their mechanical stability. We have recently developed a method to fabricate GCNTs by carbonization of HBC molecules, which are preorganized in the nanoscale channels of a porous alumina membrane as inorganic template.[8] This resulted in novel, thermally stable GCNTs with the graphene layers oriented perpendicularly to the tube axis.

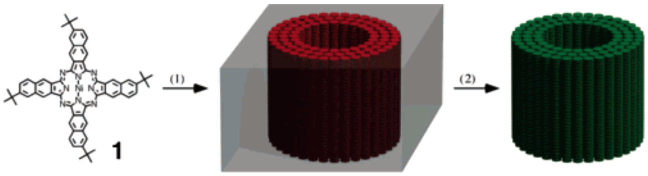
Phthalocyanines (Pcs) are well-known discotic graphenes which have served as molecular materials.[9] Compared with HBCs, commercially available Pcs supply functional centers with totally different electronic or optical properties. Although Pcs prefer to aggregate into columnar structures by $\pi-\pi$ stacking,[10] the formation of long-range, ordered aggregates is difficult. Several attempts to assemble complex Pcs into one-dimensional nanostructures by cation complexation of crown ether derivatives of phthalocyanines[11] and charge separation of a charged Pc−C_{60} complex,[12] respectively, have been reported.

Herein, we demonstrate that the pyrolysis of tetrakis(*tert*-butyl)-naphthalocyaninato nickel (Ni−BNc, compound **1**), a homologue of Pc with a larger π system, in an inorganic template leads to unprecedented types of nanotubes: (i) nanotubes with walls consisting of intact, well-aligned Nc disks; (ii) nitrogen-containing GCNTs with well-ordered columnar wall structures, and (iii) GCNTs with walls also containing metallic nickel nanoparticles.

A porous alumina membrane (Whatman, 60 μm thickness) containing straight, separated nanoscale channels was used as template (Scheme 1). The average pore size of the membrane was 200 nm (evaluated by scanning electron microscopy, SEM). Ni−BNc was loaded into the inner surface of the template pores with a THF solution of Ni−BNc (5.0 mg/mL) similar to the method previously described.[8] Ni−BNc-loaded membranes were annealed at 400 °C for different times under a nitrogen atmosphere. The template was subsequently removed with NaOH solution.

The Nc nanotubes thus prepared were straight and parallel, with lengths of up to several tens of micrometers (Figure 1a). The average diameter of the tubes was 200 nm, which matched that of the template channels. Transmission electron microscopy (TEM) demonstrated that the tubes were hollow, with a wall thickness of about 20 nm (Figure 1b). Electron diffraction clearly showed an interplanar distance of 0.34 nm along the tube axis (Figure 1b, inset), which is obviously the layer-to-layer separation of the π-stacked Nc disks. The tube walls were thus constructed from well-ordered, layered Nc disks, with the stacking of the disks parallel to the tube axis.

Scheme 1. Illustration of the Preparation of Nc Nanotubes (for clarity, the disk size has been exaggerated)[a]



[a] (1) Preorganization and thermal treatment of Ni−BNc in the template channels. (2) Removal of porous alumina template.

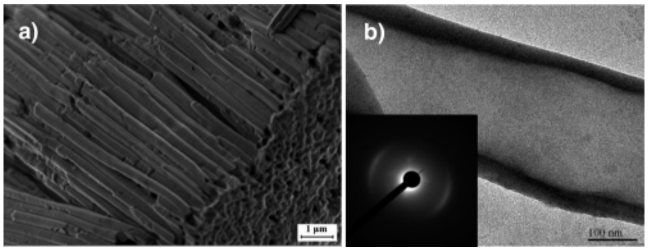


Figure 1. SEM image (a) and TEM image (b) of Nc nanotubes prepared after thermal treatment of a Ni−BNc-loaded membrane at 400 °C for 15 h with a temperature increase rate of 2 °C/min and removal of the membrane. Inset of Figure 1b shows the electron diffraction pattern of the Nc nanotube wall.

As to the mechanism of tube formation, it is important that discotic molecules form columnar structures on the alumina surface mostly by edge-on $\pi-\pi$ stacking[13] (face-on stacking occurs, in particular, when the functional groups of the discotic molecule contain oxygen[14]). It appears now that thermal treatment is important for reorganizing the Nc disks into more ordered architectures. When Ni−BNc-loaded membranes were annealed at 400 °C for 5 h or less, the columnar architectures within the formed tube walls were not highly ordered, according to the electron diffraction (ED) analysis. When the thermal treatment was conducted at 400 °C for more than 15 h, the obtained tubes showed distinctly ordered wall structures formed by $\pi-\pi$ stacking, demonstrating the significant improvement of the stacking order of the molecular disks. The tubes were still green in color because of the high thermal stability of Ni−BNc (TGA, Supporting Information) and, indeed, constructed from Ni−BNc molecular disks. The nanotubes were insoluble in THF, suggesting that some cross-linking had occurred. This can be initiated by the cleavage of *tert*-butyl groups (FTIR, Supporting Information) from the Nc disks during prolonged thermal treatment. The Nc disks were thus linked to each other to further stabilize the ordered structures. Amorphous precursors, such as hyperbranched polyphenylenes, did not lead to ordered tube wall structures.

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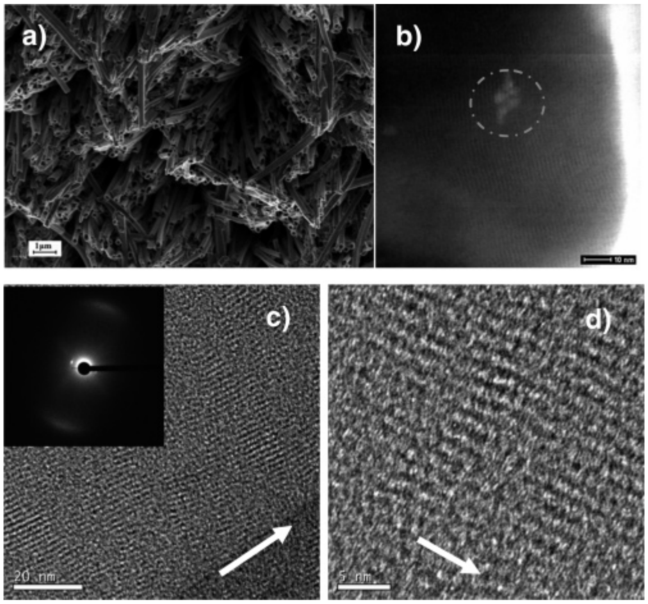

Figure 2. Carbonized Nc nanotubes prepared by thermal treatment of a Ni−BNc-loaded membrane at 400 °C for 5 h, 600 °C for 5 h, and subsequent removal of the membrane: (a) SEM image of aligned nanotubes; (b) nickel particle agglomerate (circled) surrounded by ordered columnar architectures; (c) TEM image of ordered columnar architectures of the tube wall (inset shows electron diffraction pattern of the tube wall); (d) HRTEM showing graphene disks oriented perpendicularly to the tube axis. The arrows indicate the tube axis.

Thermal treatment of the Ni−BNc-loaded membrane at 600 °C led to carbonized nanotubes (Figure 2a). The aligned nanotubes were obtained as black products, which were quickly and easily dispersed into solvent with sonication. Interestingly, the walls of the carbon nanotubes displayed highly ordered, columnar structures, which were clearly visualized with TEM (Figure 2c). Investigation of the columns under high-resolution TEM (HRTEM) indicated the alignment of disks, which were stacked efficiently and oriented perpendicularly to the tube axis (Figure 2d). Diffraction spots corresponding to 1.6 nm can clearly be seen on electron diffraction patterns (see inset in Figure 2c).[15] Smeared peaks perpendicular to the column direction correspond to a 0.34 nm distance. This suggests that the columns were constructed from stacked disks, with the distance of 0.34 nm between the disks and 1.6 nm between the neighboring columns. The distance of 0.34 nm is comparable to that of the (002) diffraction of graphite (0.335 nm). Instead of sharp dots, however, a smeared diffraction pattern was observed, suggesting that the disks were not as highly ordered as that of layers of graphite. This seems reasonable, given that the graphenes originate from the carbonization of Nc disks, which could not form long-range graphitic sheets during the stabilizing thermal treatment.

Tiny nickel crystals appeared on the surface of the tube walls or encapsulated into the wall during the carbonization process and could be seen as bright spots in a high-angle annular dark-field scanning TEM (HAADF STEM) image (Supporting Information). The average diameter of the particles is 5−10 nm. The HAADF STEM image (Figure 2b) shows an agglomerate of nickel nanocrystals on a background of ordered columnar architectures. These results suggest that aggregation of the nickel particles did not inhibit the ordered structures during the high-temperature treatment, which stabilized the graphitic structures of the tube walls.

In summary, discotic Nc molecules were used for the first time as building blocks to fabricate novel Nc nanotubes in nanoscale template channels. Thermal stabilization of the ordered columnar structures of the Ni−BNc molecules, induced from the $\pi-\pi$ interactions in the nanoscale channels of the template, resulted in Nc nanotubes with walls consisting of well-ordered Nc molecular disks. Further thermal treatment of Ni−BNc at 600 °C produced carbonized nanotubes containing ordered columnar, graphitic wall structures with the graphene disks arranged perpendicular to the tube axis. These nanotubes may be useful for extending the application of Nc molecules for nanodevice fabrication.

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Supporting Information Available: FTIR spectra of pristine and thermal treated Ni−BNc, TGA of Ni−BNc, and HAADF STEM image of carbonized nanotube prepared after pyrolysis at 600 °C. This material is available free of charge via the Internet at http://pubs.acs.org.

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